

# Effect of Oxide Additions on the Polymorphism of Tantalum Pentoxide (System $\text{Ta}_2\text{O}_5\text{-TiO}_2$ )

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The phase equilibrium relationships of the  $\text{TiO}_2\text{-Ta}_2\text{O}_5$  system were determined in air. An equimolar compound,  $\text{TiTa}_2\text{O}_7$ , was found to melt congruently at about 1662 °C and have a monoclinic unit cell  $a=20.297$  Å,  $b=3.804$  Å,  $c=11.831$  Å,  $\beta=120^\circ14'$ , apparently isostructural with  $\text{TiNb}_2\text{O}_7$ . In addition, two other compounds are postulated to occur at about  $\text{TiO}_2:49\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2:7\text{Ta}_2\text{O}_5$  and to dissociate at about 1230 and 1190 °C, respectively.  $\text{TiO}_2$  apparently accepts a maximum of 9 mole percent  $\text{Ta}_2\text{O}_5$  in solid solution at 1630 °C. Two eutectics occur in the system at 54 mole percent  $\text{Ta}_2\text{O}_5$  and 1650 °C and 31 mole percent  $\text{Ta}_2\text{O}_5$  and 1630 °C.

The high temperature form of  $\text{Ta}_2\text{O}_5$  is apparently triclinic at room temperature with  $a=3.801$  Å,  $b=3.785$  Å,  $c=35.74$  Å,  $\alpha=90^\circ54.4'$ ,  $\beta=90^\circ11.5'$ , and  $\gamma=89^\circ59.9'$ . A metastable transition occurs at 320 °C to a monoclinic form which inverts to tetragonal at 920 °C with  $a=3.81$  Å,  $c=36.09$  Å. Several intermediate morphotropic phases are found with up to 9 mole percent  $\text{TiO}_2$  in solid solution.

Key Words: Phase equilibria, polymorphism, tantalum pentoxide, titanium dioxide.

## 1. Introduction

The increased commercial importance of tantalum oxide together with the apparent ambiguity of its phase relationships have served as an impetus to investigate both the pure oxide and the interaction of  $\text{Ta}_2\text{O}_5$  with other oxides. As part of a continuing program of phase equilibria studies, it was decided to investigate the effect of various impurities and environments on  $\text{Ta}_2\text{O}_5$ . Titanium dioxide was selected to be studied in air because the cation has a radius similar in size to  $\text{Ta}^{+5}$  but differing in oxidation state. Investigations of other tantalate systems are in progress and the results will be reported subsequently.

No systematic attempt to study the phase equilibrium relationships in the system  $\text{Ta}_2\text{O}_5\text{-TiO}_2$  has been previously reported. However, some attempts to investigate the polymorphs of  $\text{Ta}_2\text{O}_5$  have been described in the literature [1–12].<sup>1</sup> The exact relationships of the various polymorphs are still in doubt because of the lack of suitable single crystals needed to properly characterize the phases. However, it has been concluded by various workers [10, 11] that  $\text{Ta}_2\text{O}_5$  has at least two structurally different polymorphs, with a reversible phase transition occurring at about  $1360 \pm 10$  °C [11].

## 2. Materials

The starting materials used in this study were found by general quantitative spectrochemical analyses to have the following impurities:

$\text{TiO}_2$ —Si present in amounts less than 0.01 percent, Cu present in amounts less than 0.001 percent, Ca present in amounts less than 0.0001 percent.

$\text{Ta}_2\text{O}_5$ —Al and Si present in amounts less than 1.0 percent; Cu and Mg present in amounts less than 0.1 percent; Ag, Ca, and Mn each present in amounts less than 0.0001 percent.

## 3. Specimen Preparation and Test Methods

Three-gram batches of various proportions of  $\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2$  were weighed, mixed in a mechanical shaker for approximately 10 min, and pressed into disks at about  $10^4$  psi. The disks were placed on platinum setters and calcined in air at 1000 °C for 16 hr. Following this preliminary heat treatment portions of the ground specimen were placed in platinum alloy tubes and heated in the quenching furnace at various temperatures for different periods of time.

The tubes containing the specimens were quenched into ice water and examined by x-ray diffraction techniques. A high-angle recording Geiger counter-

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

diffractometer and Ni-filtered Cu radiation was used in the study. The Geiger counter traversed the specimen at 1/4 deg/min. and radiation was recorded on the chart at 1 deg-2 $\theta$ /in. The unit cell dimensions reported can be considered accurate to about  $\pm 2$  in the last decimal place listed. Equilibrium was considered to have been achieved when x-ray patterns showed no change after successive heat treatments of a specimen or when the data were consistent with the results from a previous set of experiments. Solidus and liquidus temperatures were obtained by using both a quenching furnace and an induction furnace. Because of the temperature limitation of the quenching furnace, melting points above 1800 °C were determined with an induction furnace. Some duplicate determinations below 1800 °C were made using both furnace types.

The quenching furnace consisted of two concentric ceramic tubes wound with platinum-rhodium alloy wire. The inner tube served as the primary winding and the outer one as the booster. Separate power sources were used with each winding.

The power for the outer winding (booster) was supplied from a variable autotransformer. An a-c bridge type controller in which the furnace winding was one arm of the bridge was used to control the temperature of the inner winding.

The induction furnace consisted of an iridium crucible and cover which acted as the susceptor and specimen container. A small fragment of the calcined material was placed in the iridium crucible on an iridium setter or button and heated to the desired temperature for about 2 min to achieve thermal equilibrium. Apparent temperatures were measured with a calibrated, disappearing filament-type optical pyrometer which was sighted through a 45 deg calibrated prism into a viewing hole at the center of the crucible cover. The temperature measuring system of both the quenching furnace and the induction furnace were calibrated frequently against the melting point of Au (1063 °C), Pd (1552 °C), and Pt (1769 °C). In addition, the measuring system of the induction furnace was calibrated against the melting point of Rh (1960 °C). Temperatures reported in the present study are considered accurate to within  $\pm 10$  °C below 1650 °C and to within  $\pm 20$  °C above. The measurements were reproducible to within  $\pm 5$  °C, or better. The degree of melting was determined by the physical appearance of quenched or cooled specimens. The first adherence of the specimen to the platinum container or iridium setter generally established the beginning of melting. In quenched specimens, complete melting was established by the formation of a meniscus. Similarly, the slumping or loss of shape of the inductively heated specimens established complete melting.

## 4. Results and Discussion

The phase diagram, figure 1, for the system Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> in air was constructed from data in table 1 (part A, B and C). Circles represent composition and temperature of experiments conducted in the quench-

ing furnace; triangles represent those conducted with a high temperature x-ray furnace. A triangle with an arc under the base represents experiments conducted in both types of furnaces at the same temperature and a square represents those conducted in an induction furnace. Heavy dashed lines delineate regions of the phase diagram where equilibrium could not be unequivocally established by the experimental methods employed in this study.

Alternate dotted and dashed lines represent metastable equilibrium relationships on the phase diagram.

Several melting points of Ta<sub>2</sub>O<sub>5</sub> have been reported [11, 13] previously. The melting point of Ta<sub>2</sub>O<sub>5</sub> determined in this investigation was  $1887 \pm 20$  °C which is in reasonable agreement with the previously reported value of Reisman et al., [11]. The numerous reported melting points of TiO<sub>2</sub> have been tabulated by Schneider [14]. A redetermination of the melting point of TiO<sub>2</sub> was not attempted because of the inherent problems associated with the determination.

### 4.1. L-Ta<sub>2</sub>O<sub>5</sub> and Related Phases<sup>2</sup>

Brauer [1] reported a structural modification of Ta<sub>2</sub>O<sub>5</sub> which was isostructural with the low temperature form of Nb<sub>2</sub>O<sub>5</sub>. Hahn [2] listed x-ray diffraction powder data for a similar form of Ta<sub>2</sub>O<sub>5</sub>.

The x-ray diffraction pattern of L-Ta<sub>2</sub>O<sub>5</sub> is characterized by strong subcell lines and numerous weak superstructure lines. Lehovc [3] indicated that the major lines of the x-ray powder pattern for Ta<sub>2</sub>O<sub>5</sub> could be accounted for on the basis of an orthorhombic subcell  $a' = 6.20$  Å,  $b' = 3.66$  Å, and  $c' = 3.89$  Å. The powder pattern given in reference 4 failed to account for the superstructure lines on the basis of a similar size subcell. Zaslavskii [5] and Harvey and Wilman [6] on the basis of single crystal data, accounted for the superstructure lines in their respective patterns by increasing the  $b$  axis to  $b = 44.02$  Å ( $12b'$ ) and  $b = 69.6$  Å ( $19b'$ ), respectively. Frevel and Rinn [7] attempted to account for the superstructure lines of their powder pattern by selecting a monoclinic cell  $a = 7.32$  Å ( $2b'$ ),  $b = 15.55$  Å ( $4c'$ ),  $c = 10.79$  Å,  $\beta = 120^\circ 36'$ . However, Terao [8] found that his powder pattern could be indexed only by utilizing approximately twice the previous monoclinic  $c$  axis ( $c = 21.549$  Å).

The subcell of the low temperature form of Ta<sub>2</sub>O<sub>5</sub> used for this study can be indexed on the basis of an orthorhombic cell  $a' = 6.19$  Å,  $b' = 3.67$  Å,  $c' = 3.89$  Å. The various published unit cell constants [4-9], including those employed by the present authors as well as those derived by others from single crystal and electron diffraction data, failed to provide suitable  $hkl$  values to account for the superstructure reflections in the Ta<sub>2</sub>O<sub>5</sub> used in this study. Therefore, no x-ray diffraction pattern for low Ta<sub>2</sub>O<sub>5</sub> is given. Although the published  $d$ -spacings derived from the subcell of the various patterns of Ta<sub>2</sub>O<sub>5</sub> agree with those found to occur in the present work, some reflections resulting from the superstructure have not been reported previously. The variance of superstructure reflections

<sup>2</sup> L-Ta<sub>2</sub>O<sub>5</sub> represents the low temperature polymorph of Ta<sub>2</sub>O<sub>5</sub>.



TABLE 1. *Experimental data for compositions in the system TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>*  
Part A. Quenching data

Composition		Heat treatments				Results	
		Initial <sup>a</sup>		Final <sup>b</sup>			
TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	Temp	Time	Temp	Time	Physical observation	X-ray diffraction analyses <sup>c</sup>
<i>Mole %</i>	<i>Mole %</i>	°C	<i>Hour</i>	°C	<i>Hour</i>		
0	100			1220	264	Not melted.	L-Ta <sub>2</sub> O <sub>5</sub> .
				1306	16	do.	Do.
				1350	65	do.	H-Ta <sub>2</sub> O <sub>5</sub> + L-Ta <sub>2</sub> O <sub>5</sub> .
				1506	24	do.	H-Ta <sub>2</sub> O <sub>5</sub> .
				1535	4.5	do.	Do.
				1775	6	do.	Do.
1	99	1220	264	1329	336	do.	L-Ta <sub>2</sub> O <sub>5</sub> .
				1299	90	do.	Do.
				1204	72	do.	Do.
				1462	19	do.	H <sub>trt</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1506	24	do.	Do.
				1640	4.5	do.	Do.
		1506	24	1641	16	do.	Do.
				1100	432	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1155	66	do.	Do.
				1204	72	do.	H <sub>trt</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1260	112	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>trt</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1299	90	do.	Do.
2	98	1640	4.5	887	65	do.	H <sub>trt</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1461	19	do.	H <sub>trt</sub> -Ta <sub>2</sub> O <sub>5ss</sub> + "30:1" <sub>ss</sub> .
				1640	4.5	do.	Do.
				1641	19	do.	Do.
				887	65	do.	Do.
				1461	19	do.	Do.
		1640	4.5	901	67	do.	Do.
				1100	432	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1200	64	do.	"30:1" <sub>ss</sub> .
				1461	16	do.	Do.
				1506	24	do.	Do.
				1641	16	do.	Do.
3	97	1461	16	901	67	do.	Do.
				1100	432	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1155	66	do.	"30:1" <sub>ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1260	112	do.	Do.
				1471	16	do.	"30:1" <sub>ss</sub> .
				1590	20	do.	Do.
		1641	16	1641	16	do.	Do.
				901	67	do.	Do.
				1100	432	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1297	20	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1316	65	do.	Do.
				1345	65	do.	Do.
4	96	1486	16	1486	16	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> + "30:1" <sub>ss</sub> .
				1506	72	do.	Do.
				1535	4.5	do.	Do.
				1588	64	do.	Do.
				924	89	do.	Do.
				1078	72	do.	Do.
		1506	72	1104	65	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1150	16	do.	Do.
				1155	64	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1201	16	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				876	16	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				950	19	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> + "30:1" <sub>ss</sub> .
5	95	1297	20	1297	20	do.	Do.
				1351	2	do.	Do.
				800	2.5	do.	Do.
				1628	16	do.	Do.
				1097	336	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1506	72	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
		1628	16	1628	16	do.	Do.
				1097	336	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1155	60	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1628	16	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1097	336	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1628	16	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
6	94	1588	64	1643	24	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1506	24	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1055	112	do.	Do.
				1078	72	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1097	336	do.	Do.
				1104	72	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
		1628	16	1150	16	do.	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1155	64	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s).
				1201	16	do.	Do.
				1345	65	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1486	16	do.	Do.
				1504	24	do.	Do.
7	93	1535	4.5	1535	4.5	do.	Do.
				1560	168	do.	Do.
				1580	2	do.	Do.
				1640	16	do.	Do.
				1684	16	do.	Do.
				1400	6	do.	Do.
		1486	16	924	89	do.	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
				1124	65	do.	Do.
				1247	48	do.	Do.
				1400	6	do.	Do.
				1486	16	do.	Do.
				1400	6	do.	Do.

See footnotes at end of table, p. 181.



TABLE 1. *Experimental data for compositions in the system TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>—Continued*  
Part A. Quenching data

Composition		Heat treatments				Results			
		Initial <sup>a</sup>		Final <sup>b</sup>		Physical observation	X-ray diffraction analyses <sup>c</sup>		
TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	Temp	Time	Temp	Time				
Mole %	Mole %	°C	Hour	°C	Hour				
11	89	1486	16			.....do.....			
		1535	4.5	1351	16	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
		1580	2	1097	192	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).		
				1203	312	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s).		
		1580	2			.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
		1580	2	1097	192	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).		
13	89			1132	64	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
				1167	168	.....do.....	Do.		
				1197	168	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s).		
						.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
15	85			1097	168	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + 1:1.		
				1167	168	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.		
						.....do.....			
						.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
20	80			1358	7	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
				1470	16	.....do.....			
				1480	16	.....do.....			
				1486	16	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.		
				1508	16	.....do.....	Do.		
				1580	16	.....do.....			
				1640	16	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
				1687	16	.....do.....	Do.		
				1695	.5	.....do.....	Do.		
				1721	.16	Partially melted.			
				1750	.16	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + Liq.		
				1781	.16	.....do.....	Do.		
				1400	6		Not melted.		
				1470	16	1127	192	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + 1:1.
				1406	6			.....do.....	
				1480	16	1167	168	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + 1:1.
				1406	6			.....do.....	
				1486	16	924	89	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.
						1097	168	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + 1:1.
25	75			1055	112	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + 1:1.		
				1508	16	1060	19	.....do.....	Do.
						1091	120	.....do.....	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.
								.....do.....	
						1640	20	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.
						1651	.16	Partially melted.	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1 Liq.
						1687	.16	.....do.....	
						1721	.16	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1 Liq.
						1780	.16	.....do.....	Do.
								Not melted.	
30	70			1413	17	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.		
				1450	3	.....do.....	Do.		
				1576	16	.....do.....	Do.		
				1646	16	.....do.....	Do.		
				1722	1	Partially melted.	Do.		
				1400	6		Not melted.		
				1646	16	1300	16	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.
				1400	6			.....do.....	
						1612	2	.....do.....	H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> + 1:1.
						1642	0.16	.....do.....	Do.
33.33	66.67			1646	1	.....do.....	Do.		
				1652	1	Partially melted.	Do.		
				1656	0.16	.....do.....			
				1662	.16	.....do.....			
				1671	.16	.....do.....			
				1704	.33	.....do.....			
				1726	.16	.....do.....			
				1753	.16	.....do.....			
				1759	.16	.....do.....			
						Not melted.			
35	65	1400	6	1649	.16	.....do.....	1:1 + H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .		
				1656	.16	Partially melted.			
40	60	1400	6	1735	.08	Partially melted.			
				1745	.08	.....do.....			
45	55	1400	6			Not melted.			
						1388	113	.....do.....	1:1 + H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .
						1650	1	.....do.....	Do.
						1660	0.08	Partially melted.	
						1679	.16	.....do.....	1:1-Liq. + H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .
						1698	.16	.....do.....	Do.
						1722	.16	.....do.....	
						1741	.16	Completely melted.	
46	54	1400	6			Not melted.			
						1388	113	.....do.....	1:1 + H <sub>mon</sub> 'Ta <sub>2</sub> O <sub>5ss</sub> .
						1621	0.16	.....do.....	
						1651	.16	.....do.....	
						1653	.16	Partially melted.	
						1660	.16	.....do.....	
						1666	.16	.....do.....	
						1698	.16	Completely melted.	
		1708	.16	.....do.....					
46	54	1400	6			Not melted.			
						1652	.16	.....do.....	
						1662	.16	Partially melted.	
				1680	.16	Completely melted.			

See footnotes at end of table, p. 181.

TABLE 1. Experimental data for compositions in the system  $\text{TiO}_2\text{-Ta}_2\text{O}_5$ —Continued

Part A. Quenching data

Composition		Heat treatments				Results	
TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	Initial <sup>a</sup>		Final <sup>b</sup>		Physical observation	X-ray diffraction analyses <sup>c</sup>
		Temp	Time	Temp	Time		
<i>Mole %</i>	<i>Mole %</i>	<i>°C</i>	<i>Hour</i>	<i>°C</i>	<i>Hour</i>		
47	53	1400	6	1662	.16	Not melted.	
48	52	1400	6	1662	.16	Completely melted.	
49	51	1400	6	1662	.16	Not melted.	
				1662	.16	Completely melted.	
				1669	.16	Not melted.	
50	50	1406	6	1402	18	Partially melted.	1:1 + TiO <sub>2ss</sub> + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .
(1:1)		1400	6	1428	19	Completely melted.	1:1.
				1607	19	Not melted.	Do.
				1626	16	Completely melted.	Do.
				1639	0.08	Not melted.	Do.
				1656	.16	Partially melted.	Do.
				1660	19	Completely melted.	Do.
				1664	0.16	Not melted.	1:1 + Liq.
				1678	1	Completely melted.	1:1 + Liq.
				1690	3	Completely melted.	1:1 + Liq.
55	45			1400	22	Not melted.	1:1 + TiO <sub>2ss</sub> + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5ss</sub> (nonequilibrium).
				1621	0.16	Partially melted <sup>d</sup>	1:1 + TiO <sub>2ss</sub> .
				1636	.16	Partially melted.	1:1 + TiO <sub>2ss</sub> .
				1653	.08	Completely melted.	Do.
				1661	.16	Completely melted.	
				1672	.16	Completely melted.	
60	40			1403	16	Not melted.	1:1 + TiO <sub>2ss</sub> .
				1645	0.16	Partially melted.	Do.
				1648	.16	Completely melted.	Do.
				1654	.16	Completely melted.	1:1 + Liq.
				1662	.16	Completely melted.	
				1730	.16	Completely melted.	
65	35			1403	16	Not melted.	1:1 + TiO <sub>2ss</sub> .
				1606	0.16	Partially melted <sup>d</sup>	Do.
				1619	.16	Completely melted.	Do.
				1636	.16	Completely melted.	1:1 + Liq.
				1641	.16	Completely melted.	
				1647	.16	Completely melted.	
				1656	.16	Completely melted.	
66.67	33.33			1405	16	Not melted.	1:1 + TiO <sub>2ss</sub> .
				1628	0.16	Partially melted <sup>d</sup>	
				1645	.16	Completely melted.	
70	30			1405	16	Not melted.	1:1 + TiO <sub>2ss</sub> .
				1611	0.16	Completely melted.	
				1620	.16	Partially melted <sup>d</sup>	
				1624	.16	Completely melted.	
				1629	.16	Completely melted.	
				1631	.16	Completely melted.	
				1649	.16	Completely melted.	
75	25			1413	19	Not melted.	TiO <sub>2ss</sub> + 1:1.
				1420	4	Completely melted.	
				1542	19	Completely melted.	TiO <sub>2ss</sub> + 1:1.
				1569	2	Completely melted.	Do.
				1611	0.16	Completely melted.	
				1612	1	Completely melted.	TiO <sub>2ss</sub> + 1:1.
				1619	0.16	Completely melted.	
				1625	1	Partially melted <sup>d</sup>	TiO <sub>2ss</sub> + 1:1.
				1626	0.16	Completely melted.	Do.
				1633	1	Partially melted.	
				1638	0.16	Completely melted.	TiO <sub>2ss</sub> + Liq.
				1643	.16	Completely melted.	Do.
				1644	.16	Completely melted.	
				1658	1	Completely melted.	
				1689	0.16	Completely melted.	
				1700	.16	Completely melted.	
80	20			1357	16	Partially melted <sup>d</sup>	TiO <sub>2ss</sub> + Liq.
				1617	0.25	Completely melted.	Do.
				1620	.25	Completely melted.	
				1623	.25	Completely melted.	
				1626	.25	Completely melted.	
				1627	.25	Completely melted.	
				1631	.25	Partially melted.	TiO <sub>2ss</sub> + Liq.
				1642	.08	Completely melted.	Do.
				1649	.25	Completely melted.	
				1674	.08	Completely melted.	
				1694	.16	Completely melted.	
				1725	.16	Completely melted.	
				1742	.08	Completely melted.	
85	15			1303	16	Not melted.	TiO <sub>2ss</sub> + 1:1.
				1357	16	Completely melted.	
				1627	0.16	Partially melted <sup>d</sup>	TiO <sub>2ss</sub> + 1:1.
				1630	.16	Partially melted.	TiO <sub>2ss</sub> + Liq.
90	10			1303	16	Not melted.	TiO <sub>2ss</sub> + 1:1.
				1357	16	Completely melted.	
				1406	16	Completely melted.	TiO <sub>2ss</sub> + 1:1.
				1620	0.25	Completely melted.	Do.
				1624	1	Completely melted.	
				1628	0.16	Completely melted.	TiO <sub>2ss</sub> + 1:1.
				1632	1	Partially melted.	TiO <sub>2ss</sub> + Liq.
				1659	1	Completely melted.	
		1542	19	900	19	Completely melted.	TiO <sub>2ss</sub> + 1:1.

See footnotes at end of table, p. 181.

TABLE 1. *Experimental data for compositions in the system TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>—Continued*

Part A. Quenching data

Composition		Heat treatments				Results	
		Initial <sup>a</sup>		Final <sup>b</sup>		Physical observation	X-ray diffraction analyses <sup>c</sup>
TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	Temp	Time	Temp	Time		
Mole %	Mole %	°C	Hour	°C	Hour		
91	9	1357	16	1523	19	Not melted.	Do.
				1637	1	Partially melted.	TiO <sub>2ss</sub> + Liq.
				1643	0.25	.....do.....	
				1653	.16	.....do.....	
92	8			1523	19	Not melted.	TiO <sub>2ss</sub> + 1:1.
				1647	0.16	.....do.....	Do.
				1660	.16	Partially melted.	TiO <sub>2ss</sub> + Liq.
93	7			1523	19	Not melted.	TiO <sub>2ss</sub> .
				1651	19	.....do.....	Do.
				1666	19	Partially melted.	TiO <sub>2ss</sub> + Liq.
94	6			1396	1.5	Not melted.	
				1528	65	.....do.....	TiO <sub>2ss</sub> .
				1659	0.16	.....do.....	
95	5			1694	.16	Partially melted.	TiO <sub>2ss</sub> + Liq.
				1197	113	Not melted.	TiO <sub>2ss</sub> + 1:1.
				1303	16	.....do.....	TiO <sub>2ss</sub> .
				1357	16	.....do.....	Do.
				1406	16	.....do.....	Do.
				1528	65	.....do.....	Do.
				1623	2	.....do.....	Do.
				1749	0.16	Partially melted.	TiO <sub>2ss</sub> + Liq.
				1197	113	Not melted.	TiO <sub>2ss</sub> + 1:1.
				1528	65	.....do.....	TiO <sub>2ss</sub> .
96	4			1657	19	.....do.....	Do.
				1659	0.16	.....do.....	Do.
				1684	.16	.....do.....	Do.
				1700	.16	.....do.....	Do.
				1750	.16	.....do.....	Do.
				1000	.16	.....do.....	Do.
				1406	16	.....do.....	Do.
97	3						
98	2						

<sup>a</sup> All specimens were initially calcined at 1000 °C for 10 hr with heating and cooling rates of approximately 4 °C/min. Small portions of this calcine were then reheated for the designated time of one or more designated higher temperatures and generally quenched in Pt tubes.

<sup>b</sup> After the initial heat treatment(s) all specimens were reheated in Pt tubes to the indicated temperature.

<sup>c</sup> The phases identified are given greatest amount first in the order of amount present at room temperature. The phases are not necessarily those present at the temperature to which the specimen was heated.

H<sub>mon</sub>-Ta<sub>2</sub>O<sub>5</sub>—Monoclinic metastable form.

H<sub>tri</sub>-Ta<sub>2</sub>O<sub>5</sub>—Triclinic metastable form.

"30:1"—Metastable monoclinic solid solution phase occurring at about 30Ta<sub>2</sub>O<sub>5</sub>:TiO<sub>2</sub>.

H<sub>mon</sub>—A morphotropic modification of H<sub>mon</sub>-Ta<sub>2</sub>O<sub>5</sub>.

L-Ta<sub>2</sub>O<sub>5</sub> phase(s)—One or more phases with an x-ray powder diffraction pattern similar to low temp. form of Ta<sub>2</sub>O<sub>5</sub>.

1:1—TiTa<sub>2</sub>O<sub>7</sub>.

Liq.—Metastable phase which forms only from the quenched liquid and gives a characteristic but very poorly defined x-ray pattern.

ss—Solid solution.

"—"—Indicate that the exact stoichiometry is not known.

<sup>d</sup> Specimens appeared partially melted below the solidus and were interpolated to provide the best approach to binary equilibrium.

TABLE 1.

Part B: Induction furnace data

Composition <sup>a</sup>		Temp.	Observation	Composition <sup>a</sup>		Temp.	Observation
TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>			TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>		
5	95	1872	Not melted.	30	70	1861	Completely melted.
		1882	Do.			1757	Not melted.
		1891	Melted.			1766	Do.
		1850	Not melted.			1781	Do.
		1861	Partially melted.			1801	Do.
10	90	1868	Do.	35	65	1810	Partially melted.
		1882	Completely melted.			1819	Completely melted.
		1903	Do.			1762	Partially melted.
		1924	Do.			1776	Completely melted.
		1809	Not melted.			1726	Partially melted.
15	85	1821	Partially melted.	40	60	1744	Completely melted.
		1840	Do.			1735	Partially melted.
		1855	Do.			1742	Do.
		1865	Completely melted.			1757	Completely melted.
		1872	Do.			1762	Partially melted.
20	80	1840	Partially melted.	85	15	1770	Do.
		1852	Do.			1778	Do.
		1864	Completely melted.			1810	Do.
		1840	Partially melted.			1820	Completely melted.
		1850	Completely melted.			1840	Partially melted.
25	75	1860	Do.	95	5	1845	Completely melted.
		1829	Partially melted.			1860	Not melted.
		1840	Completely melted.			1875	Completely melted.
		1850	Do.				

<sup>a</sup> All specimens were initially calcined at 1000 °C for 10 hr with heating and cooling rates of approximately 4 °C/min.

TABLE 1.

Part C: High temperature x-ray diffraction experimental data for selected compositions in the system TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>

Composition		Previous heat treatment		Temp.	Results <sup>a</sup>
TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	Temp.	Time		
<i>Mole %</i> 0	<i>Mole %</i> 100	°C 1000 1220	<i>hr</i> 10 264	°C	
1	99	1000 1640	10 16	25	L-Ta <sub>2</sub> O <sub>5</sub> .
				500	Do.
				1000	Do.
				25	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> .
				270	Do.
				300	Do.
				350	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> .
				700	Do.
				750	Do.
				800	Do.
		825	Do.		
		850	Do.		
		875	Do.		
		900	Do.		
		925	Do.		
		950	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> + H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> .		
		975	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> .		
		25	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5ss</sub> .		
		125	Do.		
		200	Do.		

See footnotes at end of table, p. 182.

TABLE 1. — Continued

Part C: High temperature x-ray diffraction experimental data for selected compositions in the system  $\text{TiO}_2\text{-Ta}_2\text{O}_5$ 

Composition		Previous heat treatment		Temp.	Results <sup>a</sup>
$\text{TiO}_2$	$\text{Ta}_2\text{O}_5$	Temp.	Time		
Mole %	Mole %	°C	hr	°C	
2	98	1000 1640	10 16	250	Do.
				275	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				700	Do.
				800	Do.
				825	Do.
				850	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				875	Do.
				900	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
					$\text{H}_{\text{tri}}'\text{-Ta}_2\text{O}_{5\text{ss}} + "30:1"_{\text{ss}}$
				25	Do.
				100	Do.
				125	Do.
				150	Do.
				175	Do.
				200	$\text{H}_{\text{tri}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				225	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				600	Do.
				650	Do.
				675	Do.
				700	Do.
3	97	1000 1640	10 40	725	Do.
				750	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				775	Do.
				800	Do.
				825	Do.
				850	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				900	Do.
					$"30:1"_{\text{ss}}$
				25	Do.
				150	Do.
				175	Do.
				200	Do.
				235	Do.
				275	Do.
				300	Do.
				350	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				400	Do.
				600	Do.
				650	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				700	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
4	96	1000 1590	10 20	750	Do.
				775	Do.
				800	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
					$"30:1"_{\text{ss}} + \text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				25	Do.
				50	Do.
				200	$"30:1"_{\text{ss}}$
				300	Do.
				350	Do.
				400	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				500	Do.
				600	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				700	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				800	Do.
				900	Do.
					$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}} + "30:1"_{\text{ss}}$
				25	Do.
				200	Do.
				100	Do.
				300	Do.
5	95	1000 1486	10 16	350	Do.
				400	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				450	Do.
				500	Do.
				600	Do.
				700	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				750	Do.
				800	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				850	Do.
				900	Do.
				1000	Do.
					$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				25	Do.
				100	Do.
				200	Do.
				300	Do.
				325	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				375	Do.
				400	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				450	Do.
6	94	1000 1628	10 16	500	Do.
				550	Do.
				600	Do.
				650	Do.
				700	Do.
				750	Do.
				800	Do.

TABLE 1. — Continued

Part C: High temperature x-ray diffraction experimental data for selected compositions in the system  $\text{TiO}_2\text{-Ta}_2\text{O}_5$ 

Composition		Previous heat treatment		Temp.	Results <sup>a</sup>
$\text{TiO}_2$	$\text{Ta}_2\text{O}_5$	Temp.	Time		
Mole %	Mole %	°C	hr	°C	
7	93	1000 1563	10 230	850	Do.
				900	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}} + \text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				930	Do.
				1000	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_5$
					$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				25	Do.
				100	Do.
				200	Do.
				300	Do.
				400	Do.
8	92	1000 1628	10 16	450	$\text{Ta}_2\text{O}_{5\text{ss}}$ <sup>b</sup>
				500	Do.
				700	Do.
				900	Do.
				1000	Do.
				1100	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
					$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				25	Do.
				100	Do.
				200	Do.
9	91	1000 1628	10 16	300	Do.
				400	Do.
				450	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_5$ <sup>b</sup>
				500	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$ <sup>b</sup>
				550	Do.
				600	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				700	Do.
				800	Do.
				900	Do.
				1000	Do.
10	90	1000 1560	10 168	1100	$\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
					$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				25	Do.
				100	Do.
				300	Do.
				400	Do.
				500	Do.
				600	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$ <sup>b</sup>
				700	Do.
				800	Do.
				900	Do.
				1000	Do.
				1100	Do.
					$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$
				25	Do.
				100	Do.
				300	Do.
				400	Do.
				500	Do.
				600	$\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$ <sup>b</sup>

<sup>a</sup> L-Ta<sub>2</sub>O<sub>5</sub> — low temperature stable form of Ta<sub>2</sub>O<sub>5</sub>. $\text{H}_{\text{tri}}'\text{-Ta}_2\text{O}_5$  — a metastable triclinic form of Ta<sub>2</sub>O<sub>5</sub> with  $a \approx 3.8 \text{ \AA}$ ,  $b \approx 3.8 \text{ \AA}$ , and  $c \approx 35 \text{ \AA}$ . $\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_5$  — a metastable monoclinic form of Ta<sub>2</sub>O<sub>5</sub> related to  $\text{H}_{\text{tri}}'\text{-Ta}_2\text{O}_5$  by  $a \approx \sqrt{2} \times 3.8$ ,  $b \approx \sqrt{2} \times 3.8$ . $\text{H}_{\text{tet}}'\text{-Ta}_2\text{O}_5$  — a high temperature tetragonal modification of Ta<sub>2</sub>O<sub>5</sub>. $\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$  — a monoclinic phase related to  $\text{H}_{\text{tri}}'\text{-Ta}_2\text{O}_5$  by having a significant smaller  $\beta$  angle than  $\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_5$ . $"30:1"$  — a metastable monoclinic solid solution phase occurring at about 30Ta<sub>2</sub>O<sub>5</sub>:TiO<sub>2</sub>.

ss — solid solution.

<sup>b</sup>  $\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_{5\text{ss}}$  could not be detected in the presence of  $\text{H}_{\text{mon}}'\text{-Ta}_2\text{O}_5$  because of  $\beta$  angle similarity.addition of TiO<sub>2</sub> whereas those derived from the sub-cell appear to have essentially the same spacings.

A typical example would be a diffraction line occurring at  $26.53^\circ 2\theta$  in Ta<sub>2</sub>O<sub>5</sub> which was found to occur at  $26.24^\circ$  with 10 percent TiO<sub>2</sub> addition. Conversely, a reflection positioned at  $63.60^\circ 2\theta$  in Ta<sub>2</sub>O<sub>5</sub> appeared to move less than  $0.1^\circ 2\theta$  over the same compositional range. Some of the low angle x-ray diffraction lines, which, for a solid solution, should exhibit the least  $2\theta$  shift, actually shift more than many of the high angle lines.

The relative peak intensity of the x-ray powder patterns of specimens in this compositional range seem to show maximum intensity at 2 percent TiO<sub>2</sub>, diminishing while becoming more diffuse with increasing TiO<sub>2</sub> and sharpen up with a maximum of intensity at about 12 mole percent TiO<sub>2</sub>. These fine line differences, abnormal shifts in *d*-spacings, and intensity difference, are more characteristic of compounds than of solid solution phenomena. For these reasons, phases occurring at the approximate compositions 98Ta<sub>2</sub>O<sub>5</sub>:2TiO<sub>2</sub> ("49:1") and <sup>3</sup> 88Ta<sub>2</sub>O<sub>5</sub>:12TiO<sub>2</sub> ("7:1") are postulated in the system. Although the exact compositions of the postulated "nonstoichiometric" compounds cannot be established by x-ray powder diffraction this method is sufficient to indicate that the solid solution interpretation is unlikely. Since the stoichiometries of the compounds are not known exactly, the compounds are dashed on figure 1.

A similar phenomenon has been found to occur in other tantalate systems. For example, in the system Ta<sub>2</sub>O<sub>5</sub>-TaO<sub>2</sub>F, Jahnberg and Andersson [15] obtained single crystal data on samples of different compositions within a field which might have been interpreted as a continuous solid solution series of the L-Ta<sub>2</sub>O<sub>5</sub> type. From the single crystal data they concluded that a series of discrete compounds exist within this composition region.

Lehovec [3] described the structure of the tantalum oxide subcell with the tantalum atoms near positions (000), (1/2,1/2,0), two oxygen atoms at about (0,0,1/2) (1/2,1/2,1/2) and the other three oxygen atoms in the same plane as the tantalum atoms. He concluded that the loose packing of oxygen atoms in the plane *z*=1/2 could easily permit the diffusion of interstitial oxygen ions and/or the incorporation of interstitial cations and therefore the existence of oxides with cation/anion ratios differing from that of Ta<sub>2</sub>O<sub>5</sub>.

From x-ray powder diffraction data Moser [9] suggested that the low temperature form of Ta<sub>2</sub>O<sub>5</sub> may occur in several states. On the basis of change in *d*-values of some weak powder lines, especially the one occurring between 3.6 and 3.3 Å, he arbitrarily divided low Ta<sub>2</sub>O<sub>5</sub> into four "states"  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ , and  $\gamma_4$ .

## 4.2. H-Ta<sub>2</sub>O<sub>5</sub> and Related Metastable Phases <sup>4</sup>

Lagergren and Magneli [10] reported the existence of a high temperature polymorph occurring above 1320 °C and indexed the x-ray pattern on the basis of an orthorhombic unit cell with *a*=35.6 Å, *b*=3.79 Å, *c*=3.735 Å. Zaslavskii et al. [5], concluded from powder data that the high temperature form was tetragonal with *a*=3.801 Å, *c*=35.67 Å.

Reisman et al. [11], postulated from fine line splits in the x-ray powder diffraction pattern that the high temperature modification had a symmetry lower than orthorhombic. They further concluded that the phase transition occurred at 1360 °C, and was sluggish but completely reversible.

Laves and Petter [12] reported three polymorphic forms of high Ta<sub>2</sub>O<sub>5</sub> from x-ray and optical data. At room temperature a monoclinic form ( $\alpha''$ ) was found to occur, with *a*=3.784 Å, *b*=3.802 Å, *c*=35.82 Å, and  $\beta$ =91.00°. This polymorph was reported to undergo a phase transition at 320 °C (to  $\alpha'$ ) with *a*=*b*=5.365 Å, *c*=35.85 Å,  $\beta$ =91.00° at 400 °C. A tetragonal modification was apparently obtained with long time heating at 1450 °C which, when examined at 20 °C, was found to have *a*=3.795 Å, *c*=35.54 Å.

Franklin and Wu [16] have suggested that, from room temperature single crystal data, the high temperature form of Ta<sub>2</sub>O<sub>5</sub> can be interpreted as triclinic with *a*=7.58 Å, *b*=7.59 Å, *c*=35.71 Å,  $\alpha$ =90.23°,  $\beta$ =91.14°, and  $\gamma$ =90.12°.

### 4.2.1. H-Ta<sub>2</sub>O<sub>5</sub>

In the present investigation Ta<sub>2</sub>O<sub>5</sub> was found to exhibit an enantiotropic phase transition at about 1360±10 °C. The addition of TiO<sub>2</sub> lowers the phase transition from about 1360 to about 1150 °C at 9 mole percent TiO<sub>2</sub>. By extrapolation from high temperature x-ray data the high temperature form is postulated to be tetragonal in its stability field rather than the monoclinic or triclinic symmetry generally observed at room temperature. The symmetry of H-Ta<sub>2</sub>O<sub>5</sub> cannot be proven conclusively since the phase transition temperature is above the upper temperature limitation of the high temperature x-ray furnace used for this study.

### 4.2.2. Metastable Phases of Ta<sub>2</sub>O<sub>5</sub>

From high temperature data, Ta<sub>2</sub>O<sub>5</sub> can be shown to have a number of metastable phases occurring in the stability field of the low temperature polymorph. They are indicated on figure 1 as H<sub>tri</sub>-Ta<sub>2</sub>O<sub>5</sub>,

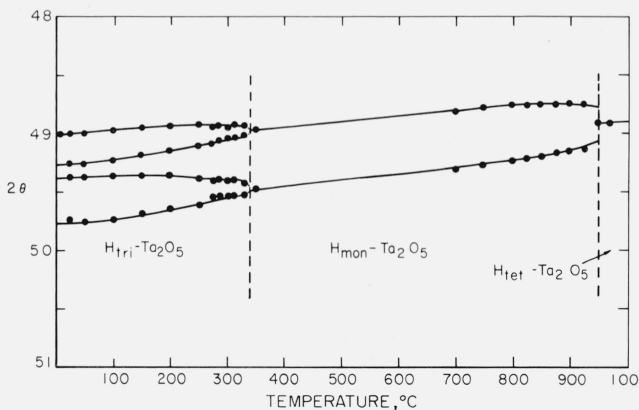


FIGURE 2. Metastable phase transitions in the high temperature form of Ta<sub>2</sub>O<sub>5</sub> (from high temperature x-ray data) (CuK $\alpha$ ).

H<sub>mon</sub>-Ta<sub>2</sub>O<sub>5</sub>, and H<sub>tet</sub>-Ta<sub>2</sub>O<sub>5</sub>. A plot of temperature versus 2 $\theta$  is shown in figure 2 for the family of peaks generated by symmetry changes for the tetragonal (1,0,17). The metastable phase assemblage of the high temperature form of Ta<sub>2</sub>O<sub>5</sub> is significantly changed by the addition of TiO<sub>2</sub> and the existence of several solid solution phases was established. They are indicated on figure 1 as 30:1<sub>ss</sub>, H<sub>mon</sub>-Ta<sub>2</sub>O<sub>5ss</sub>, and H'<sub>mon</sub>-Ta<sub>2</sub>O<sub>5ss</sub>.

<sup>3</sup> Quotation marks around a compound indicate uncertainty in the exact composition.

<sup>4</sup> H-Ta<sub>2</sub>O<sub>5</sub> represents the high temperature polymorph of Ta<sub>2</sub>O<sub>5</sub> and phases structurally related to it.

#### 4.2.2.1. $H_{tri}\text{-Ta}_2\text{O}_5$ : Room Temperature Form

$\text{Ta}_2\text{O}_5$  when quenched from above the stable 1360 °C phase transition has undergone at least two metastable phase transitions (tetragonal  $\rightarrow$  monoclinic  $\rightarrow$  triclinic). "Single crystal" precession patterns show a multiplicity of crystallites partially ordered with respect to each other. If a quenched specimen is ground lightly in a mortar and pestle the x-ray powder diffraction pattern shows diffuse peaks. However, if the specimen is carefully prepared for diffraction, with a minimum of mechanical deformation, then the diffuse peaks are resolved into fine line splittings, as previously described by Reisman et al. [11]. This room temperature x-ray diffraction powder pattern (table 2)

TABLE 2. X-ray diffraction powder data for  $H_{tri}\text{-Ta}_2\text{O}_5$  <sup>a</sup>  
( $\text{CuK}\alpha$  radiation)

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$ <sup>b</sup>	$I/I_0$ <sup>c</sup>	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$ <sup>b</sup>	$I/I_0$ <sup>c</sup>
8.93	8.93	004	6				
4.47	4.47	008	7	2.485	2.485	0 $\bar{1}$ 11	12
3.776	3.781	101	58	2.474	2.474	1 $\bar{0}$ 11	17
3.773	3.778	101	70	2.466	2.465	1 $\bar{0}$ 11	26
3.768	3.770	011	55	2.457	2.458	11 $\bar{6}$	64
3.759	3.758	011	51	2.454	2.453	11 $\bar{6}$	73
	3.624	103		2.445	2.446	0 $\bar{1}$ 11	16
3.620			30	2.436	2.437	11 $\bar{6}$	61
	3.624	013		2.433	2.433	11 $\bar{6}$	58
3.617	3.617	103	30	2.239	2.241	0 $\bar{1}$ 13	4
3.590	3.591	013	3	2.232	2.234	0 $\bar{1}$ 16	12
3.363	3.367	015	68	2.230	2.231	1 $\bar{0}$ 13	9
3.357	3.360	105	77	2.224	2.224	1 $\bar{0}$ 13	8
3.354	3.351	105	68	2.207	2.208	0 $\bar{1}$ 13	4
3.321	3.323	015	20	2.031	2.031	0 $\bar{1}$ 15	7
3.060	3.064	017	25	2.022	2.022	1 $\bar{0}$ 15	7
3.052	3.054	107	26	2.015	2.016	1 $\bar{0}$ 15	7
3.044	3.044	107	25	1.8997	1.9004	200	27
3.015	3.018	017	16	1.8915	1.8924	020	27
2.979	2.978	0 $\bar{0}$ 12	100	1.8492	1.8502	0 $\bar{1}$ 17	8
2.763	2.762	019	3	1.8417	1.8422	1 $\bar{0}$ 17	14
2.751	2.750	109	3	1.8360	1.8369	1 $\bar{0}$ 17	15
2.739	2.741	109	5	1.8257	1.8255	0 $\bar{1}$ 17	9
2.717	2.718	019	5	1.7861	1.7869	0 $\bar{0}$ 20	3
	2.578	114			1.7525	028	
2.586	2.575	114	3	1.7517			1
	2.562	114			1.7508	208	
	2.559	114		1.7461	1.7466	208	1

<sup>a</sup> Specimen of  $\text{Ta}_2\text{O}_5$  heated to 1775 °C for 6 hr and quenched.

<sup>b</sup> Relative intensity.

<sup>c</sup> Based on triclinic cell  $a = 3.801$  Å,  $b = 3.785$  Å,  $c = 35.74$  Å,  $\alpha = 90^\circ 54.5'$ ,  $\beta = 90^\circ 11.5'$ , and  $\gamma = 89^\circ 59.9'$ . (The last decimal point of the angles is given for the purpose of recalculation.)

can be completely indexed on the basis of a triclinic cell with  $a = 3.801$  Å,  $b = 3.785$  Å,  $c = 35.74$  Å,  $\alpha = 90^\circ 54.4'$ ,  $\beta = 90^\circ 11.5'$ ,  $\gamma = 89^\circ 59.9'$ . In this study, the triclinic form was found to undergo a phase transition on heating at about 320 °C to a monoclinic modification ( $H_{\text{mon}}\text{-Ta}_2\text{O}_5$ ).

#### 4.2.2.2. $H_{\text{mon}}\text{-Ta}_2\text{O}_5$

This modification is related to the triclinic form by  $a_{\text{mon}} \approx \sqrt{2}a_{\text{tri}}$ ,  $b_{\text{mon}} \approx \sqrt{2}b_{\text{tri}}$ ,  $c_{\text{mon}} \approx c_{\text{tri}}$ . This monoclinic polymorph is apparently the  $\alpha'$  phase reported by Laves and Petter [12]. At about 950 °C on heating in the high temperature x-ray furnace,  $H_{\text{mon}}\text{-Ta}_2\text{O}_5$  inverts to a tetragonal modification ( $H_{\text{tet}}\text{-Ta}_2\text{O}_5$ ).

#### 4.2.2.3. $H_{\text{tet}}\text{-Ta}_2\text{O}_5$

This tetragonal modification of  $\text{Ta}_2\text{O}_5$  may be related to the tetragonal phase ( $\alpha$ ) reported by Laves and Petter [12]. According to Laves and Petter [12] a tetragonal form was obtained at room temperature by heating  $\text{Ta}_2\text{O}_5$  for extended periods of time at

1450 °C. The high temperature (950 °C) indexed powder pattern for the tetragonal modification of  $\text{Ta}_2\text{O}_5$  is given in table 3. The pattern was indexed on the basis of a tetragonal cell  $a = 3.81$  Å,  $c = 36.09$  Å. In this study, pure  $\text{Ta}_2\text{O}_5$  could not be stabilized to room temperature. However, the stabilization could be achieved by the addition of certain impurities [17].

TABLE 3. High temperature x-ray diffraction powder data for  $H_{\text{tet}}\text{-Ta}_2\text{O}_5$  <sup>a</sup>  
( $\text{CuK}\alpha$  radiation)

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$ <sup>b</sup>	$I/I_0$ <sup>c</sup>
4.55	4.51	008	7
3.80	3.79	101	93
3.65	3.64	103	37
3.37	3.37	105	80
3.07	3.07	107	54
3.02	3.01	0 $\bar{0}$ 12	80
2.76	2.76	109	10
2.491	2.487	1 $\bar{0}$ 11	53
2.461	2.461	116	100
2.256	2.256	0 $\bar{0}$ 16	10
2.247	2.245	1 $\bar{0}$ 13	17
2.039	2.035	105	7
1.907	1.907	200	43
1.900	1.897	202	47
1.855	1.855	1 $\bar{0}$ 17	37
1.702	1.704	211	23
	1.700	1 $\bar{0}$ 19	
1.687	1.690	213	7

<sup>a</sup> X-ray taken at 950 °C.

<sup>b</sup> Based on tetragonal cell  $a = b = 3.81$  Å,  $c = 36.09$  Å.

<sup>c</sup> Relative intensity.

#### 4.2.3. Metastable Solid Solutions

##### 4.2.3.1. $H_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$

The effect of  $\text{TiO}_2$  additions was investigated by both high temperature x-ray and conventional quenching techniques. From high temperature x-ray data,  $\text{Ta}_2\text{O}_5$  accepts in excess of 7 mole percent  $\text{TiO}_2$  at 470 °C to form a metastable solid solution phase ( $H_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$ , fig. 1).

The metastable tetragonal  $\rightleftharpoons$  monoclinic transition indicated in figure 1 as continuing to temperatures above 1000 °C may possibly be stable in the field labeled  $H\text{-Ta}_2\text{O}_{5\text{ss}}$ . An ultra-high temperature x-ray study would be needed to establish the equilibrium conditions in this region.

##### 4.2.3.2. $H'_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$

The  $H_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$  phase has an apparent morphotropic phase transition to another metastable monoclinic form ( $H'_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$ , fig. 1). The monoclinic angle of  $H'_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$  apparently changes with composition and temperature, and grades into that of the other monoclinic form at about 550 °C and 9 mole percent  $\text{TiO}_2$ . The x-ray diffraction pattern for  $H'_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$  from the 9:1 composition at room temperature is given in table 4. The specimen was indexed from powder data on the basis of a monoclinic cell with  $a = 5.367$  Å,  $b = 5.368$  Å,  $c = 35.70$  Å, and



TABLE 4. X-ray diffraction powder data for the phase  
H<sub>mon</sub>'Ta<sub>2</sub>O<sub>5</sub> (10TiO<sub>2</sub>:90Ta<sub>2</sub>O<sub>5</sub>)<sup>a</sup>  
(CuK<sub>α</sub> radiation)

<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i> <sup>b</sup>	<i>I</i> / <i>I</i> <sub>0</sub> <sup>c</sup>
4.469	4.461	008	8
3.771	3.781	111	100
	3.765	$\bar{1}11$	
3.638	3.637	113	
3.596	3.593	$\bar{1}13$	
3.380	3.379	115	8
3.321	3.322	$\bar{1}15$	65
3.076	3.075	117	50
3.014	3.014	$\bar{1}17$	20
2.973	2.973	0,0,12	25
2.714	2.713	$\bar{1}19$	95
2.492	2.492	1,1,11	15
2.472	2.472	206	28
2.444	2.441	$\bar{1},1,11$	38
2.418	2.418	206	63
2.247	2.247	1,1,13	43
2.232	2.231	0,0,16	3
2.203	2.202	$\bar{1},1,13$	8
2.036	2.035	1,1,15	5
1.897	1.897	220	5
			63

<sup>a</sup> Specimen heated to 1640 °C for 16 hr and quenched.

<sup>b</sup> Based on monoclinic cell *a* = 5.367 Å, *b* = 5.368 Å, *c* = 35.707 Å and β = 91°42'.

<sup>c</sup> Relative intensity.

β = 91°42'. This phase is apparently related to H<sub>tri</sub>'Ta<sub>2</sub>O<sub>5</sub> in the following manner:

$$a_{\text{mon}} \approx \sqrt{2}a_{\text{tri}}, b_{\text{mon}} \approx \sqrt{2}b_{\text{tri}}, c_{\text{mon}} \approx c_{\text{tri}}.$$

#### 4.2.3.3. "30:1<sub>ss</sub>"

From high temperature x-ray data, another phase was found to occur from about 2.5 to 4.5 mole percent TiO<sub>2</sub> and to have a maximum dissociation temperature of about 375 °C. This metastable solid solution phase is apparently related to H<sub>tri</sub>'Ta<sub>2</sub>O<sub>5</sub> and can be indexed on the basis of a monoclinic cell *a* = 3.794 Å, *b* = 3.807 Å, *c* = 35.70 Å, β = 90°51'. This phase corresponds closely to the α'' form of Laves and Petter [12]. The indexed x-ray powder pattern for the 3 mole percent TiO<sub>2</sub> specimen is given in table 5. It should be emphasized again that the high temperature tetragonal form of Ta<sub>2</sub>O<sub>5</sub> is not quenched-in and that it is the various metastable phases which are detected when specimens are quenched from elevated temperatures and examined at room temperature by x-ray diffraction.

#### 4.3. TiO<sub>2</sub> · Ta<sub>2</sub>O<sub>5</sub>(TiTa<sub>2</sub>O<sub>7</sub>)

The intermediate compound TiO<sub>2</sub> · Ta<sub>2</sub>O<sub>5</sub> was found to occur in the system and to melt congruently at about 1662 °C. From x-ray diffraction data, table 6, the compound can be indexed on a monoclinic basis *a* = 20.397 Å, *b* = 3.804 Å, *c* = 11.831 Å, β = 120°14' and is apparently isostructural to the compound TiNb<sub>2</sub>O<sub>7</sub> reported previously by Roth and Coughanhour [18] and by Wadsley [19]. It is interesting to note that phases analogous to those compounds richer in Nb<sub>2</sub>O<sub>5</sub>

TABLE 5. X-ray diffraction powder data for the phase  
"30:1<sub>ss</sub>" (3TiO<sub>2</sub>:97Ta<sub>2</sub>O<sub>5</sub>)<sup>a</sup>  
(CuK<sub>α</sub> radiation)

<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i> <sup>b</sup>	<i>I</i> / <i>I</i> <sub>0</sub> <sup>c</sup>
4.46	4.46	008	3
3.78	3.79	011	80
	3.78	$\bar{1}01$	
	3.78	101	
	3.63	$\bar{1}03$	
3.63	3.63	013	15
3.373	3.371	$\bar{1}05$	13
3.361	3.359	015	60
3.330	3.329	105	11
3.066	3.066	$\bar{1}07$	5
3.050	3.051	017	13
3.022	3.022	107	6
2.974	2.975	0,0,12	100
2.761	2.762	$\bar{1}09$	1
2.747	2.746	019	3
2.722	2.721	$\bar{1}09$	3
2.484	2.484	$\bar{1},0,11$	6
2.469	2.470	0,1,11	15
2.451	2.459	$\bar{1}16$	50
	2.448	1,0,11	
	2.439	$\bar{1}16$	
	2.313	$\bar{1}18$	
2.313	2.313	$\bar{1}18$	2
2.241	2.240	1,0,13	2
2.231	2.231	0,0,16	6
2.227	2.227	0,1,13	4
2.210	2.209	1,0,13	2
2.030	2.030	1,0,15	2
2.018	2.018	0,1,15	2
1.9034	1.9034	020	11
1.8964	1.8967	200	13
1.8926	1.8927	022	7
1.8885	1.8891	$\bar{2}02$	3
1.8486	1.8488	1,0,17	5
1.8394	1.8386	0,1,17	8
1.8257	1.8256	1,0,17	4
1.7846	1.7848	0,0,20	2

<sup>a</sup> Specimen of 3TiO<sub>2</sub>:97Ta<sub>2</sub>O<sub>5</sub> heated to 1640 °C for 40 hr and quenched.

<sup>b</sup> Relative intensity.

<sup>c</sup> Based on monoclinic cell *a* = 3.794 Å, *b* = 3.307 Å, *c* = 35.70 Å, and β = 90°51'.

than TiNb<sub>2</sub>O<sub>7</sub> [20, 21] were not found to occur in the TiO<sub>2</sub> - Ta<sub>2</sub>O<sub>5</sub> system under the conditions studied. Two eutectics were found to occur in the system (fig. 1) at approximately 54 mole percent Ta<sub>2</sub>O<sub>5</sub> and 1650 °C and 31 mole percent Ta<sub>2</sub>O<sub>5</sub> and 1630 °C, respectively. Some difficulty was encountered in establishing the solidus curve near the higher TiO<sub>2</sub> eutectic composition since the surface of specimens quenched in this compositional region appeared glazed or partially melted below the solidus. For this reason these data were interpolated to provide the best approach to binary equilibrium. This phenomena is probably due to partial reduction in the subsolidus near the melting point of the phase assemblage. The possible deviations in stoichiometry should be investigated at higher oxygen pressures and temperatures.

#### 4.4. TiO<sub>2</sub> Solid Solutions

Titanium dioxide was found to exhibit maximum solubility of 10 mole percent Ta<sub>2</sub>O<sub>5</sub> at 1625 °C. The

TABLE 6. *X-ray diffraction powder data for*  $\text{TiO}_2 \cdot \text{Ta}_2\text{O}_5$  ( $\text{TiTa}_2\text{O}_7$ )<sup>a</sup>  
( $\text{CuK}\alpha$  radiation)

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$ <sup>b</sup>	$I/I_0$ <sup>c</sup>
10.24	10.22	001	2
9.42	9.42	201	5
5.11	5.11	002	55
5.07	5.08	401	24
4.70	4.71	402	7
4.41	4.41	400	2
3.714	{ 3.718 3.689 }	{ 110 202 }	83
3.619	3.620	111	12
3.461	3.462	401	12
3.398	{ 3.407 3.388 3.381 }	{ 003 602 111 }	100
3.317	3.317	311	12
3.297	3.298	601	12
2.949	2.946	404	12
2.866	2.865	112	38
2.754	{ 2.760 2.753 }	{ 511 512 }	48
2.725	2.723	604	14
2.658	2.657	113	38
2.560	2.556	004	7
2.540	2.541	802	5
2.507	2.508	601	23
2.427	2.426	312	5
2.390	2.389	113	7
2.312	{ 2.312 2.310 }	{ 511 605 }	51
2.290	2.289	514	19
2.047	2.044	005	38
2.039	2.039	10,0,3	25
2.006	{ 2.006 2.004 }	{ 10,0,2 515 }	5
1.9019	1.9020	020	29
1.8797	{ 1.8822 1.8777 }	{ 806 115 }	7
1.8447	1.8440	404	5
1.8185	1.8177	603	5
1.7825	1.7825	022	7
1.7621	1.7623	10,0,0	7
1.7403	1.7410	910	7
1.7178	1.7162	115	14
1.7066	1.7064	712	8
1.6939	{ 1.6940 1.6938 }	{ 12,0,4 12,0,3 }	19
1.6653	1.6658	11,1,3	29
1.6620	1.6621	807	36

<sup>a</sup> Specimen heated to 1620 °C for 16 hr and quenched.

<sup>b</sup> Based on monoclinic cell  $a = 20.397 \text{ \AA}$ ,  $b = 3.804 \text{ \AA}$ ,  $c = 11.831 \text{ \AA}$  and  $\beta = 120^\circ 14'$ .

<sup>c</sup> Relative intensity.

amount of titanium dioxide solid solution ( $\text{TiO}_{2\text{ss}}$ , fig. 1) at the solidus of 1630 °C decreases with both increasing and decreasing temperatures. The extent of solid solution was delineated by both the disappearing phase

and parametric surface methods. The  $a$  parameters in  $\text{\AA}$  for the various selected compositions used in the study are shown in figure 1.

Any discussion of the nature of the solid solution would be pure speculation; however, an investigation of the physical properties might prove enlightening in characterizing this solid solution.

## 5. Future Study

This study has established that although ions of a size similar to  $\text{Ta}^{+5}$  but with different valence apparently enter into solid solution with  $\text{H-Ta}_2\text{O}_5$  they form discrete phases with  $\text{L-Ta}_2\text{O}_5$ . However, the reasons for this type of interaction cannot be determined without a knowledge of the crystal structures of both forms. The crystal structures cannot be determined without single crystals. *Single* crystals of pure  $\text{Ta}_2\text{O}_5$  apparently cannot be grown in either of the two main polymorphic forms. We, therefore, propose that a study of other systems will be of help in determining proper compositions to be used in the growth of single crystals of phases having structures similar to the polymorphs of  $\text{Ta}_2\text{O}_5$ . Such studies are in progress and will be reported at a future date.

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